



# Identification of native charge-transfer status of p-aminothiophenol adsorbed on noble metallic substrates by surface-enhanced infrared absorption (SEIRA) spectroscopy

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## ARTICLE INFO

### Article history:

Received 4 April 2018

Received in revised form 15 June 2018

Accepted 17 June 2018

Available online 23 June 2018

### Keywords:

Adsorption

Monolayer

p-Aminothiophenol

Silver substrate

SEIRA

## ABSTRACT

p-Aminothiophenol (PATP) is a preferred molecule in research on surface-enhanced Raman scattering (SERS) because of its unique characteristics of high spectral activity, easily induced charge-transfer (CT), and sensitivity to molecular structural changes. However, some aspects are still unclear, such as the initial steady state of PATP on noble metallic substrates without strong additional excitation with incident and/or induced electromagnetic radiation. Information about the initial steady state, especially the intrinsic CT state, is of great importance to elucidate the dynamic processes of CT and/or molecular structural changes under additional excitation. To investigate the native state of an adsorbed molecule, a suitable probe method that does not disrupt the native state of the whole system, including both molecules and substrates, is required. SERS is not applied in this context because of its use of high-energy visible and near-infrared light. Herein, a low-energy probe method, surface-enhanced infrared-absorption (SEIRA) spectroscopy, is employed as a suitable method for studying the native adsorption state of PATP on silver nanoisland films. The molecular structure and adsorption state were investigated. The intrinsic CT state received particular attention by analyzing the CT-related vibration of B<sub>2</sub> modes. Using Fourier transform infrared (FTIR), transmission SEIRA and reflection SEIRA spectroscopy, we explained why the relative intensities of some bands were different under different conditions. A quasi-standing orientation of PATP adsorbed on the substrates was also confirmed. More importantly, we demonstrated that there is no perceptible CT between PATP and silver nanoisland films; in contrast, CT generally occurs in a disruptive manner in SERS. Density functional theory (DFT) calculations and the selection rules for infrared (IR) transmission and reflection-absorption spectroscopy were used to analyze the spectra throughout the paper. SEIRA proved to be an effective technique to explore the native adsorption state of molecules without the excessive external disturbance induced by excitation. The results are very important in providing insight into molecules in surface-interface chemistry, enhanced spectroscopy and photoelectronics.

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## 1. Introduction

p-Aminothiophenol (PATP) is a derivative of benzene para-substituted with an amine group (–NH<sub>2</sub>) and a sulfhydryl group (–SH). It readily binds to noble metallic substrates, such as Ag, Au, and Cu. In addition, its scattering cross-section is much larger than that of many other molecules. Therefore, PATP has been widely used as an important molecule in surface-enhanced Raman scattering (SERS) [1–4].

PATP can also be used to obtain supramolecular systems in a directed or periodic arrangement of via hydrogen bonding, halogen bonding, or π–π stacking. Thus, researchers use supramolecular systems containing PATP molecules to improve the performance of materials [5]. Moreover, because of its excellent chemical reaction properties, PATP has also been widely used in conducting films [6], heavy metal ion detection [7], electrochemical sensors [8], optoelectronics [9] and other advanced research areas. Many of these uses of PATP are performed when PATP is adsorbed onto substrates, especially noble metallic substrates. In most studies on the sensing and optoelectronic applications of PATP, its charge-transfer (CT) properties were discussed in depth. However, some information about the CT state of PATP on substrates remains unclear. And another significant question is whether the

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CT occurs between the molecule and the substrate at any energy. This problem has not yet been clearly explained. To resolve this problem and enhance the applications of PATP, we sought to study the adsorption state of PATP on silver substrates, especially the CT state. SERS is not applied in the proposed research because of the high energy levels of the incident lasers used (3.82–1.17 eV). These high energy levels subject both the molecules and the substrates to strong additional excitation through incident radiation and surface plasmon resonance. A suitable method with low energy levels and minimal disturbance of detection systems is thus still desired.

Recently, surface-enhanced infrared-absorption (SEIRA) spectroscopy has been developed as a new analytical technique and has been well applied to various research fields, such as surface-interface structures [10], catalysis [11], and electrochemistry [12], among others [13]. SEIRA refers to the 10–1000 times greater infrared (IR) absorption intensity of a molecule when it is adsorbed on a metallic layer or metallic particles such as Ag, Au, or Cu than that without metal [4, 14, 15]. Both SEIRA and SERS are types of surface-enhanced vibrational spectroscopy. Although the degree of enhancement of SEIRA is several orders of magnitude smaller than that of SERS, the IR absorption cross-section ( $10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup>) [16] is much larger than the scattering cross-section of Raman scattering ( $10^{-28}$  cm<sup>2</sup> molecule<sup>-1</sup>) [17, 18]. Thus, the sensitivity of SEIRA detection is favorable compared with that of SERS. In other words, SEIRA can also obtain signals from trace molecules in single molecular layers.

Importantly, SEIRA has several advantages over SERS in investigating molecular self-assembled monolayers. First, because SEIRA uses very low-energy IR photons as the probe (0.50–0.05 eV), SEIRA itself interferes minimally with the investigated system, especially with the molecular electronic states. In contrast, SERS uses high-energy photons from an ultraviolet, visible or near IR laser, and thus, the system is disturbed away from the initial electronic states to some extent. Second, SEIRA, which uses incident light from low-power sources, causes little disturbance to detection systems compared with SERS, which uses incident light from high-power lasers. Thus, SEIRA is very suitable to investigate the native states of adsorbed molecules. The different properties of SEIRA and SERS indicate that SEIRA is more suitable for observing the initial states of monolayer molecular assemblies on surfaces.

Regarding the intrinsic CT effect between the molecule and the substrate, SEIRA also has an advantage in direction-dependent analysis. With the transmission and reflection spectral acquisition modes, the CT can be studied in the surface-parallel and surface-normal directions, which are orthogonal. Transmission and reflection SEIRA spectral acquisition provides an opportunity for multidimensional analysis of the intrinsic CT. Moreover, together with the selection rules for IR transmission and reflection-absorption spectroscopy, SEIRA can also be used to identify the orientation of molecules on substrates. Therefore, SEIRA is a powerful and reliable tool to detect molecular states and the interactions between molecule and the Ag films when the molecules adsorbed on Ag surface [14, 19].

Density functional theory (DFT) theoretical calculations are well accepted as a useful method to predict molecular structures and the corresponding spectral information [20–22]. In this paper, we performed DFT calculations at the B3LYP/6-311++G(D) level to simulate molecular structures. All IR spectra obtained experimentally were accurately assigned by referring the results of the theoretical calculations. Based on analysis of the experimental results and the theoretical calculations, we found that PATP on silver nanoisland films is in a quasi-standing orientation. More importantly, we demonstrated that in the native adsorption state of PATP, there is no perceptible CT between PATP and the silver nanoisland films in either the surface-parallel or surface-normal direction. That is, in contrast to SERS, which often induces electron transfer because of strong excitation with light and/or excited local electromagnetic fields, there is no obvious electron transfer in the native molecular assembly. This strategy elucidates the intrinsic electronic states of PATP and provides a powerful means of investigating the

intrinsic nature of self-assembled monolayers. The conclusion in this study is of great benefit to analysis of surface-related phenomena in photoelectronics, plasmonics, catalysis and sensing.

## 2. Experimental Section

### 2.1. Chemicals

PATP and poly(diallyldimethylammonium chloride) (PDDA) (20 wt %, molecular weight of 200,000–350,000) were purchased from Sigma-Aldrich Inc. China. Potassium bromide (KBr) powder was obtained from Tianjin Guangfu Fine Chemical Co., Ltd. Silver nitrate (AgNO<sub>3</sub>) (99%) and trisodium citrate (98%) was purchased from Shanghai Chemical Reagent Co., Ltd. Other chemicals (ethanol, acetone, and chloroform) were obtained from Beijing Chemical Reagent Plant. All the chemicals were analytical grade and were used without further purification. De-ionized water ( $18.6$  M $\Omega$ ·cm<sup>-1</sup>) was obtained via a Milli-Q plus system (Millipore) and was used throughout the present study.

### 2.2. Preparation of Silver Nanoparticles (AgNPs)

AgNPs were prepared according to our previous work [23]. In a typical synthesis, 36 mg of AgNO<sub>3</sub> was dissolved in 200 mL of water in a flask. This aqueous solution was then heated to a boil under stirring and refluxed. Trisodium citrate solution (4 mL, 1:1, w/v) was added to the flask and allowed to react for 1 h. Finally, AgNPs were obtained.

### 2.3. Preparation of Samples for IR and SEIRA Measurements

KBr pellets containing PATP powder were prepared for IR transmission mode measurements. The reflection SEIRA spectra were obtained from molecular assemblies on Ag substrates. The preparation process is as follows: Glass slides (1 × 1 cm) were cleaned by sonicating in water, ethanol, acetone, chloroform, acetone, ethanol, and water successively, each for 2 min. Then, a silver film of 20  $\mu$ m thickness was evaporated on the glass slides by using a vacuum evaporation method. These slides were suspended in a PDDA solution (0.5 wt%) for 30 min. Then, the glass slides were removed, washed and dried. AgNP solution (30  $\mu$ L) was dropped onto the glass slides. Then, these glass slides were immersed in an ethanol solution of PATP at a concentration of 10<sup>-2</sup> M for 12 h. Next, the glass slides were removed, washed and dried. Thus, the sample for reflection SEIRA was obtained successfully. The samples for transmission SEIRA were prepared in a similar way to the reflective ones. The difference is that KBr plates were used to replace the Ag-coated glass slides. The AgNP-coated KBr plates were immersed in a 10<sup>-2</sup> M PATP ethanol solution for 12 h. Next, the KBr plates were removed, washed and dried, after which they were ready for transmission SEIRA measurement. The three types of spectral measurement configurations are illustrated in Fig. S1 in the supporting information.

### 2.4. Characterization

Fourier transform infrared (FTIR) transmission spectra of the PATP powder and assembled monolayers were recorded by using KBr pellets or plates at room temperature with a Bruker VERTEX-80v vacuum FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector at a resolution of 4 cm<sup>-1</sup>. IR reflection-absorption spectroscopy spectra were recorded at a resolution of 4 cm<sup>-1</sup> at room temperature by using the A513 accessory of a Bruker VERTEX 80v vacuum spectrometer equipped with a mercury cadmium telluride (MCT) detector.

### 2.5. Theoretical Calculations

All the geometries obtained in this study were optimized by the DFT method of B3LYP, which is the hybrid of Becke's three-parameter exchange functional with the Lee-Yang-Parr correlation functional. The

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